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Short Communication

Vanadyl complexes of some tridentate dibasic Schiff bases

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Abstract

The vanadyl complexes of the type [VO.L. $(H_2O)_2$] were synthesised with 0-(N-α-Pyrrolideneimino) ethane sulphonic acid (H_2PE), 2-(N-α-pyrrolideneimino) benzene sulphonic acid (H_2PB), 0-(2-Pyrrolideneimino) benzoic acid (H_2PBA), and 3-(2-pyrrolideneimino) propionic acid (H_2PP) have been studied potentiometrically by Calvin's extension of Bjerrumn's method in aqueous media at 25°, 35° and 45° C. These chelates were also synthesised in the solid state and were characterised by elemental analysis, molecular weight, magnetic susceptibility measurements and electronic and i.r. spectral studies.

Key words: Vanadyl complexes, potentiometric studies.

1. Introduction

The vanadyl complexes of the Schiff bases H_2PE, H_2PB, H_2PBA and H_2PP obtained by the condensation of Pyrrole-2-carboxaldehyde with taurine, orthanilic acid, anthranilic acid and β-alanine, respectively have not been studied[1,2]. These Schiff bases containing acidic (-COOH or $-SO_3H$) and azomethine (-C=N) groups are structurally similar and are thus expected to behave as dibasic tridentates. This is borne out by the results communicated in this note.

2. Experimental

All the Schiff bases and their solid VO(II) chelates were prepared by the procedure reported[3] earlier. The apparatus and the reagents employed were the same as shown in an earlier communication[4].

Calvin's extension of Bjerrum's method was adopted to determine the dissociation constants of the ligands and stability constants of their vanadyl complexes. The ligands were titrated with standard alkali in the absence and in the presence of the metal-ion at 25°, 35° and 45° C. The concentration of the VO^{2+} and the ligand (H_2PE, H_2PB, H_2PBA and H_2PP) solutions were $2\cdot5 \times 10^{-3}$ M and $5\cdot0 \times 10^{-3}$ M, respectively and the pH range involved in potentiometric titration was from 3·15 to 6·30 at 25° C.

3. Results and discussion

The melting points, dissociation constants (PK_1 and PK_2) of H_2PE, H_2PB, H_2PBA and H_2PP and stability constants ($\log K_1$ and $\log K_2$) of their vanadyl complexes at 25°, 35° and 45° are summarised in Table I. Since the first constant for the formation of $VOOH^+$ is quite high, it is likely that mixed hydroxy complexes may be produced at higher pH values. Since the pH value range in the titration is between 3·15 and 6·3, the results have been interpreted assuming that there is no mixed hydroxy complex formation. It is also assumed that only mono-nuclear complexes are formed. A perusal of Table I also indicates that the stability constants increase with increase in temperature.

Table I

Melting points, dissociation constants of H_2PE, H_2PB, H_2PBA and H_2PP and stability constants of their VO(II)–complexes

Ligand/ Complex	Melting point (C°)	Dissociation stability constants	Average values		
			25°	35°	45°
H_2PE	210	pK_1	7·73	7·45	7·17
		pK_2	9·39	9·00	8·64
H_2PB	172	pK_1	3·39	3·06	2·99
		pK_2	10·32	10·06	9·81
H_2PBA	180	pK_1	3·89	3·83	3·70
		pK_2	9·10	9·02	8·92
H_2PP	175	pK_1	8·91	8·81	8·68
		pK_2	10·12	10·01	9·89
VO(II)–H_2PE	–	$\log K_1$	10·80	11·15	11·25
		$\log K_2$	8·30	8·70	8·85
VO(II)–H_2PB	–	$\log K_1$	9·65	7·80	8·00
		$\log K_2$	7·05	7·23	7·37
VO(II)–H_2PBA	–	$\log K_1$	8·43	8·62	8·79
		$\log K_2$	5·54	5·58	5·64
VO(II)–H_2PP	–	$\log K_1$	14·10	14·18	14·27
		$\log K_2$	9·30	9·45	9·57

The values of overall changes in free energy ($\triangle G$), enthalpy ($\triangle H$) and entropy ($\triangle S$) accompanying chelation have been evaluated by standard thermodynamic relations (Table II). The values of all the complexes are more negative at higher temperatures. $\triangle H$ values are positive which suggest the existence of some steric strain around the metal ion in the chelates due to fused rings. The entropy term is favourable for the complex formation as is evident from the positive values of $\triangle S$.

All the solid vanadyl complexes under study were found to be paramagnetic as suggested by their magnetic moments (Table II). It is apparent from the magnetic moments of these complexes that there is no metal-metal bonding; hence no spin exchange occurs and they exist as monomers. The data including the molecular weight, elemental analysis, magnetic moments (Table II) are based on the assumption of mononuclear complex formation.

The thermogravimetric analysis of the vanadyl complexes indicate a weight loss at 120-180° corresponding to two water molecules. On further heating a gradual loss in weight due to slow decomposition of the complex was observed, but on heating between 380° and 440°, a sudden loss in weight was recorded and metallic oxide was obtained as the end product.

Elemental analysis and molecular weight determination of all the VO(II)-complexes gave their composition as $[VO.L.(H_2O)_2]$ having 1 : 1 (metal-ligand) stoichiometry.

The absorption spectra of all the four vanadyl complexes in donor and non-donor solvents exhibit two bands in the narrow ranges 11100–11600 cm^{-1} ($\epsilon = 106$–115 mole^{-1} cm^{-1}) assignable to the transitions[5] $^2B_2 \rightarrow {}^2E_1$ and $^2B_2 \rightarrow {}^2B_1$, respectively in an octahedral environment of VO(II)[6].

Table II

Thermodynamic parameters of the vanadyl complexes of some Schiff bases

Complex	$-\triangle G$ (K.Cal/mole)			$\triangle H$ (K.cal/ mole)	$\triangle S$ (Cal/deg/ mole)	μ_{eff} B.M. at 308° K	Mol.wt.
	25°	35°	45°				Found (Calcd.)
VO(II)-H$_2$PE	25·98	28·57	29·05	21·63	159·4	1·66	287 (303)
VO(II)-H$_2$PB	20·04	21·25	22·46	14·52	116·2	1·68	338 (351)
VO(II)-H$_2$PBA	19·01	20·10	21·63	9·57	160·3	1·67	301 (315)
VO(II) H$_2$PP	19·36	20·16	20·88	4·20	143·9	1·65	258 (267)

Table III

I.R. spectra data (in cm^{-1})

Compound	ν(NH)	ν(COOH)	ν(C = O)	ν(C=N)	ν(SO_3H)	ν(M–O)	ν(M–N)
H_2PE	3180	..	..	1610	1160	..	..
VO–H_2PE	..	..	..	1600	..	505	410
H_2PB	3155	..	..	1620	1180	..	..
VO–H_2PB	..	..	..	1610	..	510	405
H_2PBA	3190	2570	1690	1625	..	..	..
VO–H_2PBA	..	..	1675	1610	..	515	400
H_2PP	3170	2585	1680	1615	..	..	..
VO–H_2PP	..	..	1660	1600	..	500	410

The results of i.r. studies are summarized in Table III.

Based on the above evidence VO(II) chelates may display an octahedral steriochemistry.

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